

GROUP CONTRIBUTIONS FOR AN ESTIMATION OF PARTIAL MOLAR VOLUMES AT INFINITE DILUTION FOR AQUEOUS ORGANIC SOLUTES AT EXTENDED RANGES OF TEMPERATURE AND PRESSURE¹

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ABSTRACT

Experimental data on the partial molar volume at infinite dilution in water for two groups of organic solutes (derivatives of benzene and aliphatic hydroxyl derivatives) measured using a vibrating-tube densimeter in the temperature and pressure ranges 298 – 573 K and 0.1 - 30 MPa are summarized. Smoothed values of partial molar volume as a function of temperature and pressure are employed for the evaluation of group and structural contributions. The contributions are used to estimate the partial molar volumes at infinite dilution in water for various solutes. Average deviation between partial molar volumes calculated from the contributions and the experimental data employed for the evaluation of the contributions is less than $1 \text{ cm}^3 \cdot \text{mol}^{-1}$ in most cases. Predictions of partial molar volumes of solutes not included in the evaluation of the contributions are performed and results are compared with experimental data.

KEY WORDS: aqueous solutions; group contribution; partial molar volume; infinite dilution.

1. INTRODUCTION

Partial molar volume at infinite dilution in water (standard partial molar volume) is a property that is essential in a process to obtain solute standard chemical potential in wide ranges of temperature and pressure. A systematic study of selected organic solutes is in progress in our laboratory. Large set of experimental data is already available and thus a development of a group contribution method for estimation of partial molar volumes is possible. Estimation methods for partial molar volumes published in the literature (e.g., recent paper by Lepori and Gianni [1]) are limited mostly to the temperature 298.15 K and atmospheric pressure. Here we present an attempt to develop a simple group contribution method for estimation of standard partial molar volumes in extended ranges of temperature.

2. EXPERIMENTAL DATA

In the course of several past years partial molar volumes at infinite dilution in water of solutes of the aromatic series (benzene and its mono- and di-substituted derivatives) have been systematically studied in our laboratory. A vibrating-tube densimeter [2] designed for measurements in the temperature range 298 – 573 K and at pressures up to 30 MPa was used for measurements. Data for phenol [2], cresols [3], dihydroxybenzenes [4], aniline [5], benzoic acid and its hydroxyderivatives [6] and aminoderivatives [9], toluidines [7], chlorophenols [8], *o*-phenyldiamine [9], nitrobenzene and nitrophenols [10], and *m*-aminophenol, benzonitrile and *o*-cyanophenol [11] have been already published. This study has been completed by measurements of aqueous benzene and toluene [12]. Recently a systematic investigation of some phenyl derivatives of aliphatic solutes (as intermediate solutes between aromatic and aliphatic series) and aliphatic solutes (mono- and polyhydric alcohols) [13] has been launched. In the present study data for phenylmethanol and 1-alkanols from methanol to 1-butanol only are included. List of solutes is presented in Table 1 below along with temperature ranges of experimental data. Data for several solutes do not cover entire temperature range due to decomposition at higher temperatures.

Above mentioned experimental data [2-13] for 35 organic solutes were obtained for particular pairs of temperature and pressure. Empirical function of temperature and pressure was employed to smooth the data for each solute. Values of partial molar volume along the saturation curve of water (i.e., at saturated vapor pressure of water) were calculated from the function and used to evaluate group contributions. Therefore one variable (temperature) only is assumed below.

3. GROUP CONTRIBUTION METHOD

Design of a group contribution method depends on both the molecular structures to be described and the amount of available data. Generally, data for more compounds allow more detailed set of groups and vice versa. With respect to available data the following groups are defined:

C₆H₄ (aromatic ring with four hydrogen atoms); -H ; -CH₃; -CH₂-, -OH; -NH₂; -NO₂; -Cl; -COOH; -CN. Contributions of substituent groups are assumed to be the same when

bonded to the aromatic ring and in aliphatic derivatives. Our data for di-substituted aromatic derivatives show, however, that while 1,3- and 1,4- (*m*- and *p*-) isomers have nearly identical values of partial molar volumes (mostly within the experimental uncertainty), partial molar volumes of 1,2- (*o*-) isomers differ from those of 1,3- and 1,4-isomers. Therefore a structural contribution is introduced for each substituent group (except for hydrogen) for 1,2- isomers, i.e., totally seven structural contributions: *o*-CH₃, *o*-OH, *o*-NH₂, *o*-NO₂, *o*-Cl, *o*-COOH, and *o*-CN. Partial molar volume is expressed as

$$V^0 = \sum_i N_i (G_i + S_i) \quad (1)$$

where N_i is a number of groups of type i in a molecule, G_i is the volume of the group (group contribution) and S_j the volume of structural contribution. For example the partial molar volume of *o*-cresol (1-hydroxy-2-methylbenzene) is expressed as $G(\text{C}_6\text{H}_4) + \{G(\text{CH}_3) + S(o\text{-CH}_3)\} + \{G(\text{OH}) + S(o\text{-OH})\}$ while those of *m*- and *p*-cresol are $G(\text{C}_6\text{H}_4) + G(\text{CH}_3) + G(\text{OH})$. Non-branched aliphatic chains are constructed from -CH₃ and -CH₂- groups and therefore the group contribution of hydrogen atom, $G(\text{H})$, is related only to hydrogen bonded to the aromatic ring.

Values of group and structural contributions were evaluated using the weighted least-squares method. Objective function was defined as

$$\Phi(G, S) = \sum_k w_k (V_{k, \text{exp}}^0 - V_{k, \text{calc}}^0)^2, \quad G = \{G_i\}, \quad S = \{S_j\} \quad (2)$$

where $V_{k, \text{exp}}^0$ is the experimental value of partial molar volume of k -th solute and $V_{k, \text{calc}}^0$ is its value calculated from equation (1). Statistical weights w_k were derived from estimated experimental uncertainties δV_{exp}^0 as $w_k = 1 / (\delta V_{k, \text{exp}}^0)^2$. Uncertainties of resulting values of group and structural contributions were estimated from a covariance matrix.

4. RESULTS

4.1. Group and structural contributions

Calculations with the entire set of above defined contributions revealed that structural contributions $S(o\text{-Cl})$ and $S(o\text{-CN})$ are zero within the estimated uncertainty in the whole temperature range. The results of the consequent evaluation of ten group contributions and remaining five structural contributions ($S(o\text{-Cl}) = S(o\text{-CN}) = 0$) for temperatures in the range 273 – 573 K are shown in figure 1. Group contributions increase with increasing temperature except for the contributions of two hydrophilic groups (-OH and -NH₂). Structural contributions are small and moderately dependent on temperature except for *o*-COOH. Temperature ranges for -COOH, *o*-COOH and *o*-NO₂ contributions are limited up to about 500 K since the respective solutes decomposed at higher temperatures and data are not available.

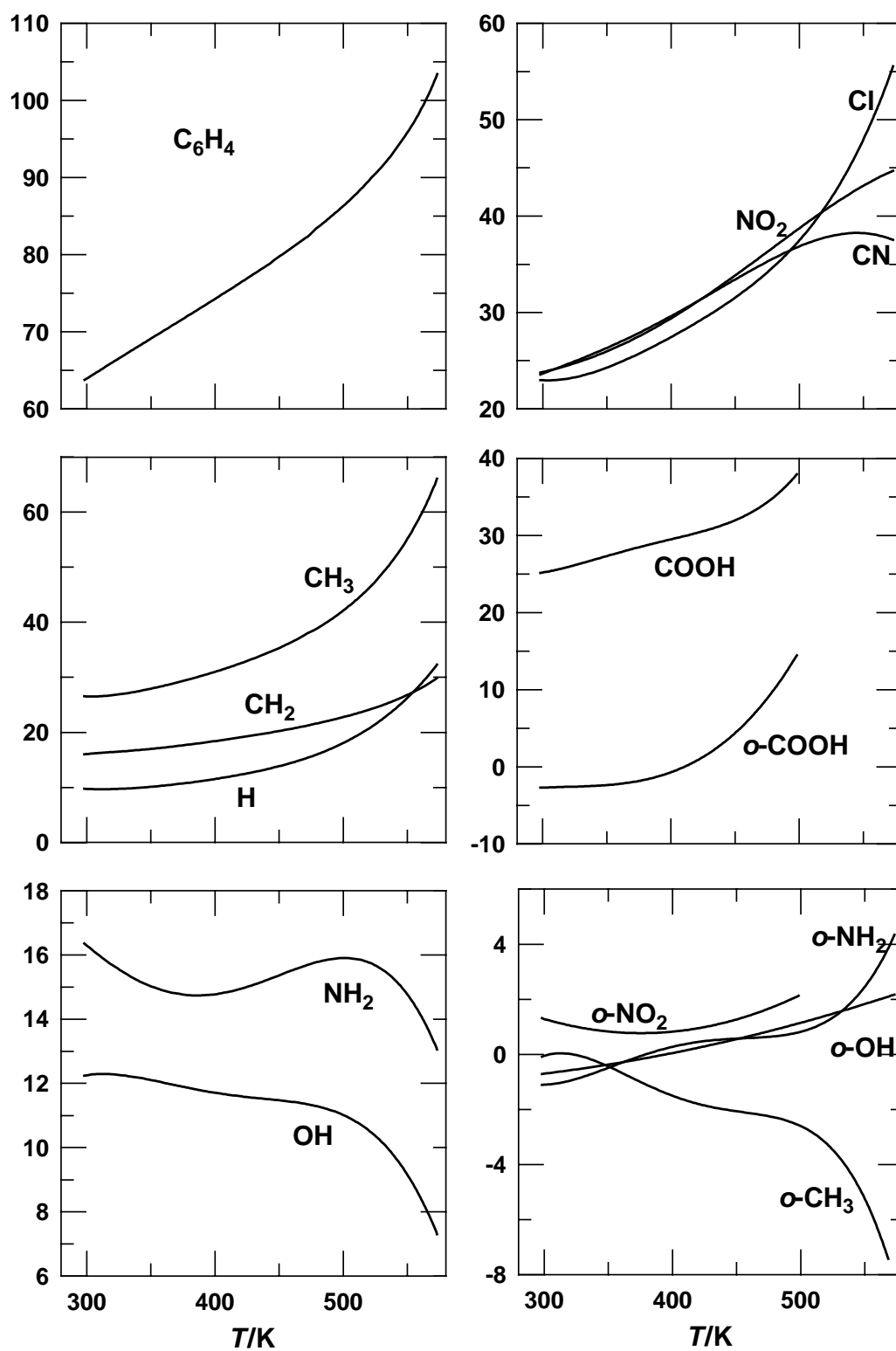


Fig.1. Dependencies of group and structural contributions on temperature. The scales of vertical axes are in $\text{cm}^3 \cdot \text{mol}^{-1}$.

Deviations of partial molar volumes calculated using group and structural contributions from experimental values are presented in Table 1 for solutes the data of which were used for the evaluation of contributions. The highest positive deviation is $5.3 \text{ cm}^3 \cdot \text{mol}^{-1}$ (3-hydroxybenzoic acid at 498 K), the highest negative deviation is $-3.2 \text{ cm}^3 \cdot \text{mol}^{-1}$ (4-hydroxybenzoic acid at 498 K). This extreme deviations are observed at the upper limit of the experimental temperature range which indicates that decomposition of the solutes might occur even at this temperature. Lowest value of RMSD ($0.12 \text{ cm}^3 \cdot \text{mol}^{-1}$) is observed for 1,3-dihydroxybenzene and 1-amino-2-methylbenzene, the highest RMSD ($1.39 \text{ cm}^3 \cdot \text{mol}^{-1}$) for 3-hydroxybenzoic acid. Average RMSD deviation over all 35 solutes is $0.50 \text{ cm}^3 \cdot \text{mol}^{-1}$.

4.2. Prediction of partial molar volumes

Predictive ability of the method was examined by a comparison of partial molar volumes calculated for solutes not included in the data set employed for evaluation of contributions with selected experimental data. Experimental data used for a comparison were mostly taken from papers that present data compilations [1, 14, 15] and from few other papers [16, 17, 18]. Some data were obtained recently in our laboratory (2-phenylethanol, phenylethanoic acid, 1,2,3-trihydroxybenzene, 1,4-dihydroxy-2-methylbenzene, 1,2-benzenedicarboxylic acid, 1,2,4-benzenetricarboxylic acid). Data for 2-phenylethanol, phenylethanoic acid, and 1,2-benzenedicarboxylic acid were not included in the evaluation of contributions since the measurements are not completed and data are available at temperatures up to 408 K only.

Predicted partial molar volumes are compared in Table 2 with values taken from the literature. Agreement observed for benzene derivatives is quite satisfactory except for solutes with the carboxyl group. Probable reason can be seen in the fact that no data for a solute with two carboxyl groups in 1,2- position were included in the data set employed for evaluation group and structural contributions. The effect of intramolecular interaction of two large $-\text{COOH}$ groups would probably lead to different structural contribution $S(o\text{-COOH})$. Despite the fact that the group contribution $G(\text{COOH})$ was evaluated from aromatic solutes only, it gives reasonable predictions for aliphatic carboxylic acids, at least at lower temperatures (see Table 2). Estimates for higher members of 1-alkanol series and for polyhydric aliphatic derivatives are mostly in satisfactory agreement with experimental values at 298 K except for 1,2,3-propanetriol. Here the vicinity of three hydroxyl groups plays a role.

Tentative predictions were made for several other aliphatic solutes (amino derivatives, acetonitrile, chloromethane). The estimates are systematically higher than experimental data. No data for aliphatic solutes with the groups $-\text{NH}_2$, $-\text{CN}$, and $-\text{Cl}$ were included in the evaluation of the contribution and thus the disagreement is not surprising. Future modifications of the method would definitely include introduction of separate group contributions for groups bonded to benzene ring and to aliphatic chains. Need for new experimental data is obvious.

Table 1. Ranges of deviations, root mean square deviations (RMSD), biases (average deviations) of values of partial molar volume calculated using group and structural contributions from experimental data.
 T_{max} is the highest temperature of experimental data, $T_{min} = 298$ K.

Solute	Deviations		RMSD	Bias	T_{max}	Solute	Deviations		RMSD	Bias	T_{max}	
	from	to					from	to				
												$\text{cm}^3 \cdot \text{mol}^{-1}$
						K						
benzene	-2.20	0.23	0.45	-0.29	573	2-hydroxybenzoic acid	-1.30	1.90	0.89	-0.36	443	
methylbenzene	-2.50	1.40	1.09	-0.70	573	3-hydroxybenzoic acid	-0.80	5.30	1.39	0.13	498	
hydroxybenzene	-1.10	-0.27	0.28	-0.65	573	4-hydroxybenzoic acid	-3.20	0.57	0.74	-0.37	498	
aminobenzene	-1.20	0.38	0.41	-0.63	573	1-hydroxy-2-chlorobenzene	-0.46	0.60	0.27	0.30	573	
benzoic acid	-0.07	3.70	0.91	0.45	473	1-hydroxy-4-chlorobenzene	-0.72	1.60	0.56	-0.13	573	
chlorobenzene	-0.98	0.97	0.51	-0.17	573	1-hydroxy-2-nitrobenzene	-1.60	0.14	0.36	-0.11	523	
nitrobenzene	-1.20	1.80	0.97	0.42	573	1-hydroxy-3-nitrobenzene	-1.50	0.26	0.50	-0.50	573	
cyanobenzene	-0.13	0.30	0.14	0.09	573	1-hydroxy-4-nitrobenzene	-0.56	0.88	0.42	0.19	548	
1-hydroxy-2-methylbenzene	-0.53	1.40	0.29	0.08	573	1-hydroxy-2-cyanobenzene	-0.38	0.70	0.27	-0.11	498	
1-hydroxy-3-methylbenzene	-1.20	0.29	0.30	-0.14	573	2-aminobenzoic acid	-0.56	1.10	0.60	0.30	498	
1-hydroxy-4-methylbenzene	-0.71	0.54	0.30	0.02	573	3-aminobenzoic acid	-2.10	0.96	0.96	-0.17	498	
1,2-dihydroxybenzene	-2.20	0.54	0.63	-0.03	498	1,2-diaminobenzene	-0.59	0.51	0.34	0.00	573	
1,3-dihydroxybenzene	-0.57	-0.10	0.12	-0.30	498	phenylmethanol	0.18	4.50	1.11	1.90	573	
1,4-dihydroxybenzene	-0.44	0.27	0.16	0.10	498	methanol	0.36	2.20	0.51	0.86	573	
1-amino-3-hydroxybenzene	-1.30	0.34	0.44	-0.21	573	ethanol	-0.61	-0.02	0.15	-0.18	573	
1-amino-2-methylbenzene	-0.26	0.30	0.12	-0.08	573	1-propanol	-1.20	-0.01	0.31	-0.29	573	
1-amino-3-methylbenzene	0.03	1.70	0.38	0.47	573	1-butanol	-0.60	0.13	0.21	-0.38	573	
1-amino-4-methylbenzene	-0.16	0.83	0.36	0.34	573							

Table 2. Comparison of partial molar volumes calculated from group and structural contributions, $(V^0)_{calc}$, with literature data, $(V^0)_{lit}$. Estimated uncertainties $s((V^0)_{calc})$ were calculated from uncertainties of contributions.

Solute	T	$(V^0)_{calc}$	$s((V^0)_{calc})$	$(V^0)_{lit}$	$calc-lit$
	K	$\text{cm}^3 \cdot \text{mol}^{-1}$			
ethylbenzene	298	116.07	0.80	114.50	1.57
propylbenzene	298	132.07	0.89	131.00	1.07
2-phenylethanol	298	117.74	0.89	117.36	0.38
	408	136.00	0.89	133.90	2.10
phenylethanoic acid	298	114.66	0.80	114.61	0.05
	408	135.50	0.80	132.80	2.70
1,2,3-trihydroxybenzene	298	87.87	1.20	87.95	-0.09
	408	98.75	1.20	98.21	0.54
1,3,5-trihydroxybenzene	298	90.71	0.89	92.10	-1.39
1,4-dihydroxy-2-methylbenzene	298	104.23	1.06	104.65	-0.42
1,2-benzendicarboxylic acid	298	108.65	0.89	114.91	-6.26
	408	134.50	0.89	131.70	2.80
2,6-dimethylbenzoic acid	298	126.69	1.20	132.60	-5.91
1,2,4-benzenetricarboxylic acid	298	124.05	1.06	129.02	-4.97
	373	142.30	1.06	143.30	-1.00
methane	298	36.32	0.57	37.30	-0.98
	573	98.33	0.86	106.00	-7.67
ethane	298	53.13	0.57	52.90	0.23
propane	298	69.13	0.69	67.00	2.13
1-pentanol	298	102.80	0.98	102.40	0.40
1-hexanol	298	118.80	1.06	117.56	1.24
1-heptanol	298	134.80	1.13	133.40	1.40
1,2-ethanediol	298	56.48	0.80	54.60	1.88
1,2-propanediol	298	72.48	0.89	71.22	1.26
1,3-propanediol	298	72.48	0.89	71.89	0.59
1,2,3-propanetriol	298	74.16	1.06	70.95	3.21
1,4-butanediol	298	88.48	0.98	88.35	0.13
1,5-pentanediol	298	104.50	1.20	104.30	0.20
	521	142.06	1.20	138.20	3.86
ammonia	298	26.11	0.57	24.85	1.26
	573	45.35	0.86	49.60	-4.25
hydrazine	298	32.70	0.57	30.13	2.57
1,2-diaminoethane	298	64.70	0.80	62.88	1.82
1,3-diaminopropane	298	80.70	0.89	78.83	1.87
1,4-diaminobutane	298	96.70	0.98	93.60	3.10

Table 2. (continued)

Solute	T	$(V^0)_{calc}$	$s((V^0)_{calc})$	$(V^0)_{lit}$	$calc-lit$
	K	$\text{cm}^3 \cdot \text{mol}^{-1}$			
methanoic acid	298	34.92	0.57	34.70	0.21
ethanoic acid	298	51.72	0.57	51.90	-0.18
	373	57.63	0.47	57.26	0.37
	473	72.20	0.92	67.69	4.51
propanoic acid	298	67.72	0.69	67.90	-0.18
	373	75.22	0.57	74.99	0.23
	473	93.48	1.13	89.41	4.07
butanoic acid	298	83.72	0.80	84.60	-0.88
pentanoic acid	298	115.71	0.98	116.00	-0.29
acetonitrile	298	50.13	0.57	47.40	2.73
chloromethane	298	49.56	0.57	46.20	3.36

5. CONCLUSION

The results show that the proposed simple additivity scheme yields reasonable results even in a wide range of temperature from ambient up to 573 K. Despite the fact that aromatic solutes were limited to mono- and di-substituted benzene derivatives, the prediction of partial molar volumes of tri-substituted benzene derivatives is satisfactory. Few solutes of aliphatic series were included in this study. Future measurements will extend the experimental data set and therefore a reformulation of the group contribution method will be possible which may improve its descriptive and predictive capabilities.

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